

Carbon Dioxide Sensor Using N,N-Dimethylaminoethyl Methacrylate and Methyl Methacrylate Copolymer

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N,N-dimethylaminoethyl methacrylate (DMAEM)-methyl methacrylate (MMA) copolymers with several different compositions were prepared by γ -ray irradiation. The sorption of carbon dioxide on the copolymer was measured by the frequency change of the 4 MHz quartz oscillators coated with the copolymers. Carbon dioxide sorption on the DMAEM-MMA copolymer was characterized by the dual sorption model (Henry type and Langmuir type). The fraction of Henry-type sorption is the smallest for the copolymer with 0.1 DMAEM mole fraction. A fast-response sensor could be fabricated when a copolymer with 0.1 DMAEM mole fraction was used.

1. Introduction

Recently, there have been increasing demands for the monitoring and control of environmental gases such as carbon dioxide, carbon monoxide and oxygen. This study deals with DMAEM-MMA copolymer as a sensing material for carbon dioxide.

It was reported previously that the copolymer of DMAEM and MMA has favorable characteristics for fabrication of an acetic acid sensor because of its fast response and stability, and it was also reported that the quartz microbalance method is useful in the low-concentration range.⁽¹⁾ Yoshikawa *et al.* have investigated the selective permeation of carbon dioxide through synthetic membranes of DMAEM/acrylonitrile (AN) copolymer.⁽²⁾

In the present study, the sorption and desorption of carbon dioxide on several different DMAEM-MMA copolymers having amino groups were examined by the quartz microbalance method in order to develop a sensor that can detect carbon dioxide.

2. Materials and Methods

DMAEM-MMA copolymers having various compositions were prepared by the following process. DMAEM and MMA monomers were purified by distillation under reduced pressure. The chemical structure of DMAEM is shown in Fig. 1. The distillation conditions were 70 mmHg at 110°C for DMAEM and 40 mmHg at 35°C for MMA. Acetone solutions of mixtures of various compositions of DMAEM and MMA monomers were sealed in glass ampouls in vacuum. These glass ampouls were irradiated with γ -rays to copolymerize the monomers. After copolymerization, each copolymer was precipitated in water and soaked in distilled water for 12 h and separated from the water by decantation. After separation, the copolymer was rinsed with distilled water for 2 h then spread on a clean Teflon film and dried at room temperature. After the purification, white or semi-transparent DMAEM-MMA copolymers were obtained. The compositions of the copolymers were determined by elemental analysis, and are listed in Table 1. Twenty mg of each copolymer was dissolved in 4 ml of acetone. Five μ l of the solution was coated on a 4 MHz quartz oscillator with a micropipette and then dried.

Illustrations of the structure of the quartz oscillator and the measurement apparatus are shown in Fig. 2. A quartz oscillator coated with a copolymer was set in the measuring cell in the thermostat. Carbon dioxide gas was introduced in the cell and its concentration was controlled by the mass flow controller. The amount of sorbed carbon dioxide in the copolymer was measured as the frequency change of the quartz oscillator using a universal counter and was estimated using the Sauerbrey equation.⁽³⁾

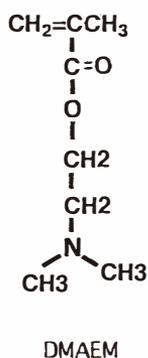
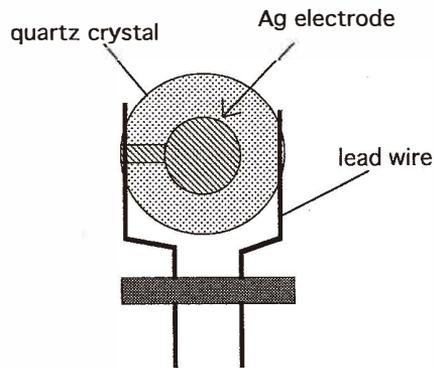


Fig. 1. Chemical structure of DMAEM.



Structure of the quartz oscillator

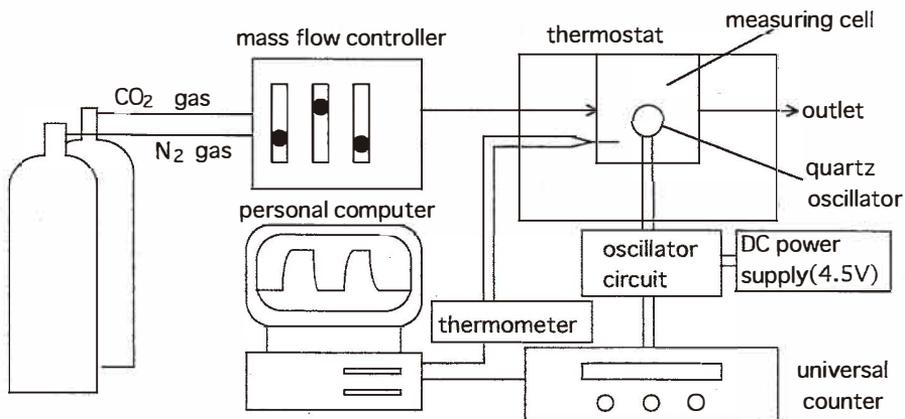


Fig. 2. Illustrations of the structure of the quartz oscillator and the measurement apparatus.

$$\Delta m = \frac{S \cdot \Delta F}{2.3 \times 10^{-6} \times F^2}$$

Δm : the mass change by the sorbed carbon dioxide (g)

ΔF : the change in frequency (Hz)

S : electrode area of quartz oscillator (cm²)

F : basic frequency of quartz oscillator (Hz)

Table 1
Dual sorption parameters.

Sample No.	DMAEM mole fraction	$k_D^{1)}$	$C_H^{2)}$	$b^{3)}$
1	0.0144	0.0966	22.0	0.282
2	0.0699	0.342	22.6	0.277
3	0.0714	0.722	23.2	0.275
4	0.0957	0.860	23.5	0.275
5	0.113	0.891	23.6	0.274
6	0.133	0.889	23.9	0.270
7	0.201	0.922	24.1	0.195
8	0.255	0.938	25.1	0.161
9	0.355	1.01	25.9	0.110
10	0.441	1.21	26.1	0.105
11	0.454	1.20	26.2	0.101
12	0.526	1.83	26.2	0.0990
13	0.553	1.97	26.3	0.0583
14	1.0	2.57	26.8	0.0323

1) mg/g copolymer · atm

2) mg/g copolymer

3) atm⁻¹

3. Results and Discussion

When the partial pressure of carbon dioxide was changed stepwise (0, 0.2, 0.4, 0.6, 0.8, and 1.0 atm), the amount of carbon dioxide sorbed on the DMAEM-MMA copolymer changed, as shown in Fig. 3. The relationship between the amount of carbon dioxide sorbed in DMAEM-MMA copolymer and the mole fraction of DMAEM in each copolymer under 1.0 atm carbon dioxide at 30°C is shown in Fig. 4. As the DMAEM mole fraction increases, the amount of sorbed carbon dioxide decreases. This finding suggests that the carbon dioxide molecule cannot be sorbed homogeneously, but is localized in the copolymer. This was confirmed by measurement of the relationship between frequency change due to coating, which is proportional to the thickness of the copolymer, and the amount of carbon dioxide sorbed in 1 g of DMAEM-MMA copolymer (mole fraction of DMAEM: 0.526), as shown in Fig. 5. This result indicates that the sorption of carbon dioxide is localized around the surface of the copolymer film.

It was confirmed that MMA does not sorb carbon dioxide in the bulk because only a very thin film of MMA coated on the quartz oscillator sorbs carbon dioxide and the measured value was unreproducible. Therefore, the dimethylamino group in DMAEM plays an important role in the sorption of carbon dioxide. The relationship between the number of carbon dioxide molecules sorbed on the DMAEM monomer unit and the mole fraction of DMAEM is shown in Fig. 6. This shows that as the mole fraction of DMAEM

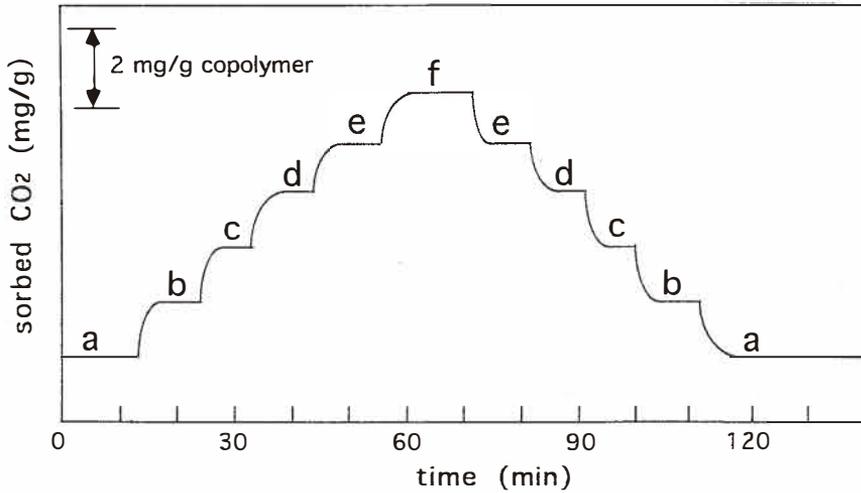


Fig. 3. The change of the amount of sorbed carbon dioxide with different carbon dioxide partial pressures: (a) 0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 1.0 atm; temperature, 30°C; flow rate, 200 ml/min.

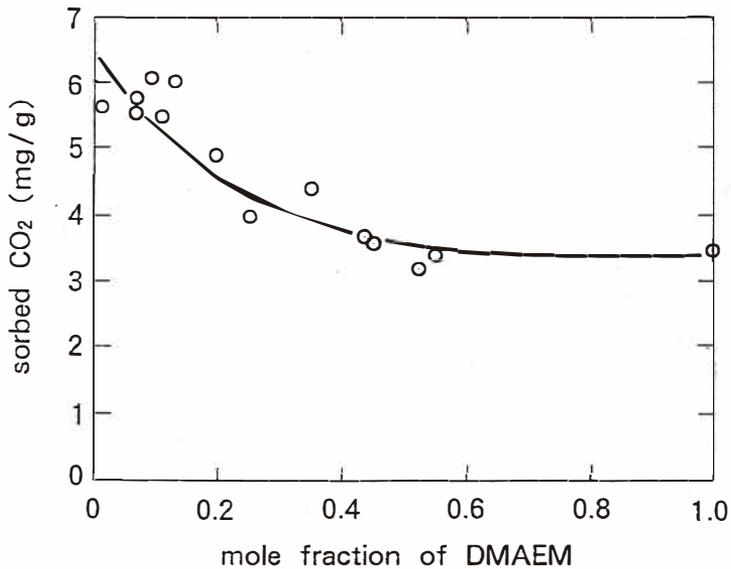


Fig. 4. The relationship between the amount of sorbed carbon dioxide per 1 g of copolymer and the mole fraction of DMAEM.

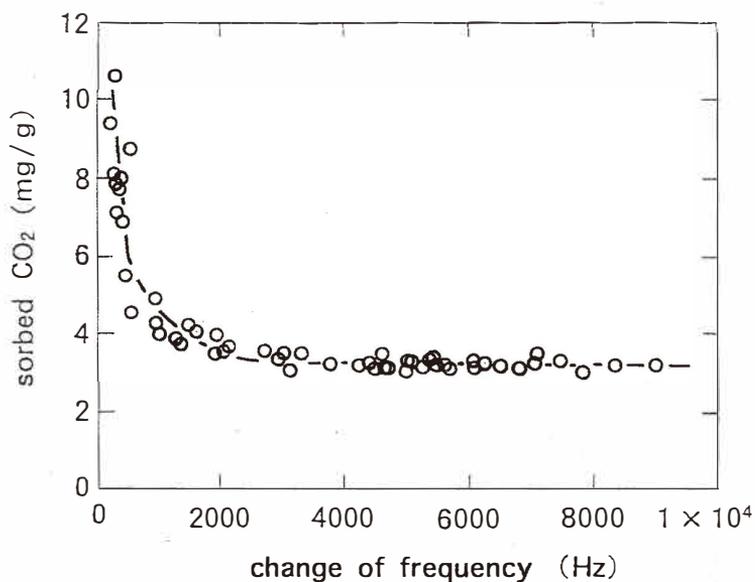


Fig. 5. The relationship between the frequency change and the amount of sorbed carbon dioxide (mole fraction of DMAEM: 0.526).

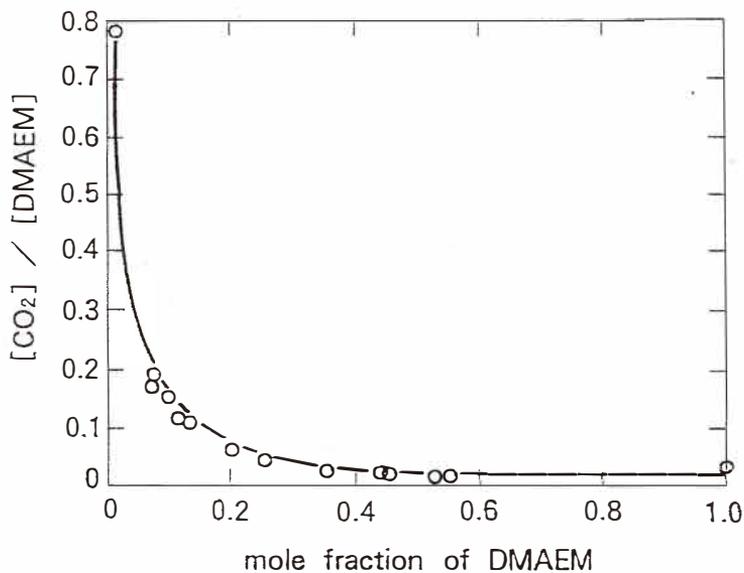


Fig. 6. The relationship between the number of carbon dioxide molecules sorbed on the DMAEM monomer unit and the mole fraction of DMAEM.

increases, the number of carbon dioxide molecules sorbed on the DMAEM monomer unit decreases. It can be presumed that as the mole fraction of DMAEM decreases, the distance between dimethylamino groups becomes greater, resulting in an increase in the number of the effective sorption sites.

The time dependence of the sorption of carbon dioxide was measured using the quartz oscillator coated with the copolymer exhibiting frequency change of about 2000 Hz when the partial pressure of carbon dioxide was changed from 0 to 1.0 atm. The length of time necessary to reach 90% of the final value of sorption was obtained for each copolymer. An example of such is shown in Fig. 7. Figure 8 shows a plot of 90% response time against the mole fraction of DMAEM of the copolymers. This plot has a minimum point around the mole fraction of 0.1. This indicates that carbon dioxide molecules can easily penetrate into the copolymer with a low mole fraction of DMAEM, and be quickly sorbed in the polymer because the distance between the sorption sites is long. However, when the mole fraction of DMAEM decreases below 0.1, the response time becomes longer. This result is expected because it is difficult for the carbon dioxide molecule to penetrate into the bulk of MMA since carbon dioxide has little affinity to MMA in the bulk.

The sorption isotherm was obtained for each copolymer. And an example is shown in Fig. 9. The dual sorption model was applied to this plot, and it was found that all sorption isotherms can be expressed by^(4,5)

$$C = C_D + C_H$$

$$= k_D \cdot p + \frac{C_H \cdot b \cdot p}{(1 + b \cdot p)}$$

C : total concentration of sorbed carbon dioxide

C_D : concentration of sorbed carbon dioxide described by Henry's Law

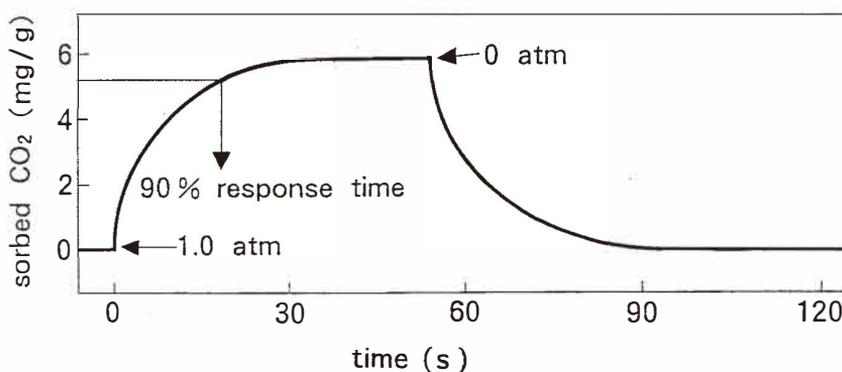


Fig. 7. The time dependence of the sorption of carbon dioxide (mole fraction of DMAEM: 0.0144).

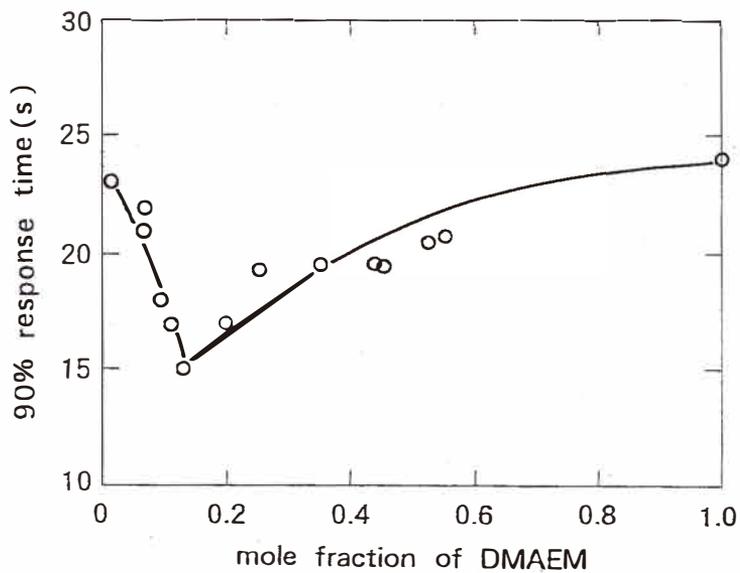


Fig. 8. The relationship between 90% response time and the mole fraction of DMAEM.

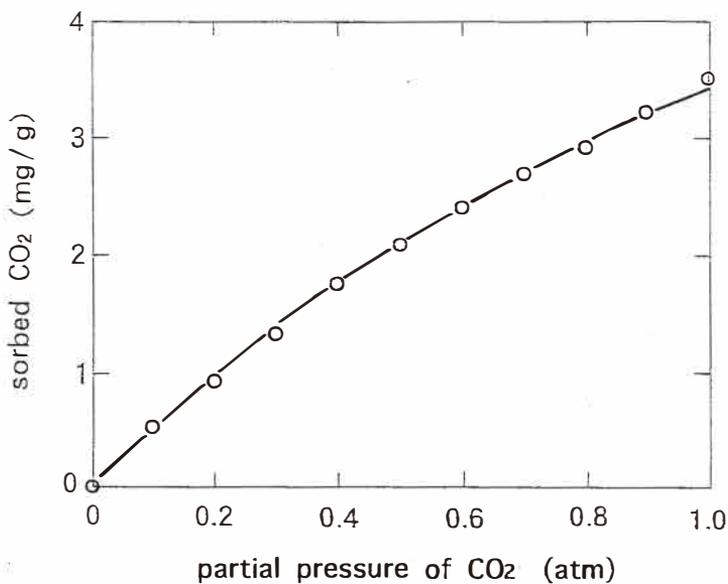


Fig. 9. The sorption isotherm of a copolymer (mole fraction of DMAEM: 0.454).

C_H : concentration of sorbed carbon dioxide described by Langmuir's Law

k_D : Henry's Law parameter

b : affinity of the carbon dioxide for microvoid

C_H : microvoid capacity constant for the Langmuir sorption

p : partial pressure of carbon dioxide.

The dual sorption parameters were determined from a plot of $1/(C - k_D \cdot p)$ vs $1/p$ and a least-squares method. The parameters are shown in Table 1. From Table 1, the fraction of Henry-type sorption C_D/C was calculated and plotted against the DMAEM mole fraction in Fig. 10. This result is in agreement with Fig. 8. Figures 8 and 10 show that the response time becomes longer when the fraction of Henry-type sorption increases. There is a minimum point around the DMAEM mole fraction of 0.1 in Fig. 10.

4. Conclusions

The carbon dioxide sorption isotherms of DMAEM-MMA copolymers were characterized using the dual sorption model. It was found that a carbon dioxide sensor having the shortest response time ever can be realized if a copolymer containing 0.1 mole fraction of DMAEM is used.

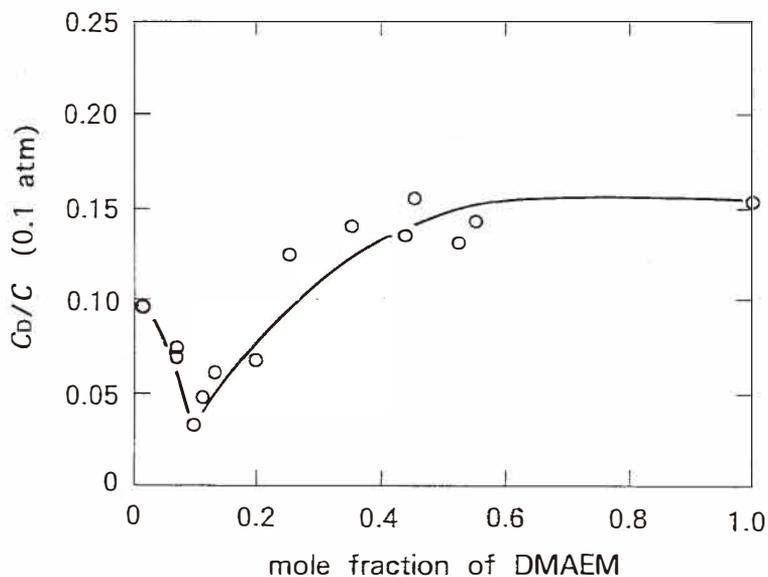


Fig. 10. The relationship between Henry's Law ratio (C_D/C) and the mole fraction of DMAEM.

To enable practical applications, the cross sensitivities of these copolymers must be measured systematically with respect to H₂O, SO₂ and NO₂.

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